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In Situ Treatment of Hazardous Material Spills in Flowing Streams

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. It documents the studies conducted to evaluate the effectiveness of two methods of applying activated carbon treatment to flowing watercourses which have been impacted by spills of hazardous materials. As such it serves as a reference to those in state, local and Federal Agencies, the transportation and chemical industries, and others who are interested in the control of spills of hazardous materials. The project is part of a continuing program of the Oil and Hazardous Materials Spills Branch, IERL-Ci, to assess and mitigate the environmental impact of pollution from hazardous material spills.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Two methods of applying activated carbon adsorption treatment to flowing streams were evaluated under comparable conditions. The first involved sub-surface introduction of bouyant carbon into the water column followed by the floating of the carbon to the surface and subsequent removal using conventional surface skimming techniques. The second involved the addition to the water of non-bouyant granular activated packaged in porous fiber bags ("tea bags") which were attached to floats. The bags were allowed to travel with the spill plume for a given distance and were subsequently removed manually. Controlled field experiments using n-hexone as the test chemical were conducted at various flow rates in a specially modified abandoned irrigation channel at the Energy Research and Development Administration's Hanford site and showed that for "low-flow" non-turbulent conditions the bouyant carbon technique was more effective in removing the chemical from the water with only tolerable amounts of the carbon remaining in the stream. As the flow and turbulence increased the pollutant removal effectiveness of the "tea bag" approach improved.

This report was submitted in fulfillment of Contracts Nos. 68-03-0330 and 68-03-2006 by Battelle-Northwest under the sponsorship of the U.S. Environmental Protection Agency.

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SECTION 1

INTRODUCTION

The use of activated carbon for in situ treatment of hazardous material spills has been reported previously.[1-4,6] The two major alternatives presently under development are the use of buoyant carbons and the use of commercial grade sinking carbons packaged in porous fiber bags attached to floatation devices. Both systems have shown promise with respect to specific applications in spill situations.

BUOYANT CARBON

Initial work with buoyant activated carbon involved media development, delivery package development, and field demonstration of the technique.[2] A commercially available granular carbon, Nuchar C-190, was found to display the desired buoyancy properties as produced. Subsequent laboratory tests confirmed that delivery could be achieved if ballasted packages could be devised that would release the media upon reaching the bottom of the receiving water. Three feasible alternatives were identified: containment in weighted plastic bottles, containment in unfired clay containers, and incorporation with gravel ballast in an ice matrix. In the first case, release of the media occurs through the narrow mouth of the bottle. Ballast contained in the bottom of the bottle holds the bottle in an upright position to allow the media to be released. Release of the media from the other packages occurs upon disintegration of the clay container in water or melting of the ice cake. All three delivery packages are considered potential alternatives at the present time.

Field demonstration was conducted using activated carbon contained in weighted plastic bottles. A total of 835 lbs (380 Kg) of carbon was applied to a simulated spill of 78 lbs (35 Kg) of an emulsifiable oil solution of an organophosphate pesticide in a ten million gallon water storage basin. The bottles of carbon and ballast were dropped into the spill area from a helicopter. Carbon was subsequently collected at the surface through use of an oil containment boom and pumped as a slurry to a storage tank. Analysis of pretreatment and posttreatment water samples taken in the spill zone showed that approximately 80 percent of the pesticide was removed from the water. Carbon recovery with a standard oil boom exceeded 90 percent.

SINKING CARBON

Preliminary work with sinking carbons was directed to the development of application techniques, and the optimization of adsorption kinetics. The former was achieved through construction of bags from open weave nylon fabric which was sufficiently tight to hold granular carbon (8 x 30 mesh) and yet allow a maximum amount of water to flow through the bag. Individual bags were suspended from floats and placed in contact with contaminated water. Tests in static tanks revealed that adsorption is exceedingly slow in the absence of turbulence. Hence, performance in lakes and backwaters would not be good unless wave action or artificial mixing were prevalent. On the other hand, the presence of currents could increase removal efficiency greatly. Indeed, small scale testing in a race track configuration revealed high levels of removal during a three hour contact time.

PURPOSE OF THESE STUDIES

Early studies of both the buoyant and sinking carbon systems were focused largely on concept development and limited testing in ponded waters. Historical data, however, indicate that a preponderance of spills occur in flowing waters. Dawson and Stradley have estimated that 82 percent of all freshwater spills occur in rivers and streams.[5] Of the remaining 18 percent, some spills will actually involve reservoirs on navigable waterways. It was the purpose of these studies to evaluate the two most promising in situ treatment techniques operable in flowing waters. Of particular interest with regard to the use of buoyant activated carbon were several technical issues: the need (or lack thereof) for ballast and packaging; the efficiency of contact; probability of unsightly carbon buildup along stream banks; and the efficiency of spent carbon collection. If the need for ballast were eliminated as a result of media suspension sponsored by natural turbulence, delivery systems could be greatly simplified. The major question to be resolved with respect to sinking carbon was the ability of natural currents to supply sufficient turbulence to enhance the kinetics of adsorption.

The work reported herein was performed under two separate contracts with the U. S. Environmental Protection Agency and was directed to the evaluation of both buoyant and sinking activated carbon systems in flowing streams. All work was conducted in a simulated flowing stream maintained on the Hanford Atomic Energy Reservation. Early studies to verify the potential for application of floating carbon without ballast were followed by parallel evaluations of the two systems under varying conditions.

SECTION 2

CONCLUSIONS

The removal of a soluble organic hazardous material from a flowing stream environment has been demonstrated by two different approaches -- one utilizing buoyant activated carbon, and one employing sinking carbon in porous fiber bags suspended from floats. The following conclusions are based on results of these studies.

BUOYANT ACTIVATED CARBON

- Buoyant carbon can be effectively employed on flowing streams without the use of ballasted packages. Carbon can be applied directly to the surface or slurried and injected beneath the surface.

- Natural turnover is sufficient to provide intimate contact of carbon with contaminated water in shallow streams.

- Floating carbon was capable of achieving 50 percent removal, at a carbon to contaminant ratio of 10:1 under the range of flow rates and spill conditions studied.

- Some floating carbon was captured in eddies and debris along the side of the water body, but carbon recovery is generally in excess of 90 percent. Containment booms must be placed in a quiescent stretch where velocity components will not exceed the capabilities of the device. Simple oil booms are sufficient if weather and current conditions allow operation.

POROUS FIBER BAGS

- Porous fiber bags can be effectively applied to spills in flowing streams, but removal is directly related to the turbulence and current structure in the receiving water. Removal rose from insignificant levels at low flow rates to 20 percent at a flow rate of 15 cubic feet (425 liters) per second.

- Fiber bag efficiency appears to be limited by kinetic considerations. Removal may improve with longer contact times than those which can be achieved in the test facility employed here.

- Up to 25 percent of the fiber bags were lost during the tests as a result of shore capture and snagging in shallow areas. This effect diminished with higher steam velocities.

- Fiber bags can be collected after use with simple booms or a wire strung perpendicular to the flow just below the surface of the stream. Positioning in a quiescent stretch is not required.

- Fabric for the fiber bags must be carefully selected to avoid decomposition by the material being removed. At the same time, use of a heat and pressure resistant material allows regeneration in the bag, thus avoiding the necessity for empty and refill sequences.

- Steam stripping was found to be an adequate method of regeneration for the methyl isobutyl ketone employed in this study.

COMPARATIVE EVALUATIONS

- Buoyant carbon was superior to porous fiber bags in terms of removal efficiency under the spill and flow conditions tested.

- Little difference between methods with respect to media loss along shorelines was noted, but fiber bags can be retrieved more simply than buoyant carbon and under more extreme flow conditions.

- Fiber bags can be loaded, unloaded, and handled with greater ease than buoyant carbon.

- Both approaches rely heavily on the ability of the response team to locate and trace the movement of the contaminant plume.

- The ability to inject slurried buoyant carbon at depth renders this approach more attractive than fiber bags for use in deeper channels.

- Buoyant carbon will be more greatly affected by adverse weather conditions than will fiber bags.

- Both approaches may be difficult to apply to very large spills simply as a result of the logistics of ferrying large quantities of carbon to the site.

SECTION 3

RECOMMENDATIONS

- A survey should be conducted to assess the availability of buoyant carbons for use in spill response.
- An air deliverable slurry injection system should be developed and tested for routine application of buoyant carbon to spills.
- A study of the treatment effectiveness of porous bag packaged carbon should be performed at a site where longer contact times than were possible for these tests can be achieved.
- Further work should be conducted to develop remote sensing and/or other techniques for the identification, location, and monitoring of spills. Some consideration should also be given to the development of methods for marking spill plumes.
- A decision framework is needed to determine when spill response is warranted and what the most effective means of response is for specific spills on a real-time basis.

SECTION 4

THE FLOWING STREAM TEST FACILITY

All tests were conducted in the Flowing Stream Test Facility (FSTF) which is an abandoned irrigation canal located on the Atomic Energy Commission Reservation at Hanford, Washington. The partially cement-lined canal was taken out of operation some thirty-four years ago when the federal government appropriated the land. Since 1973, however, it has been the subject of renovation efforts aimed at equipping it for use as a model stream for hazardous materials spill research.

For the purposes of the work reported here, renovation largely consisted of efforts to provide and control the flow of water. Two nearby wells were deepened, reactivated, and fitted with gasoline driven pumps capable of producing 200 and 600 gallons (757 and 2271 liters) of water per minute, respectively. Aluminum and "transite" irrigation pipes were installed to carry water to a reservoir formed in the upper 1000 feet (305 meters) of the canal by the construction of a permanent weir with a screw-controlled drop gate. This reservoir is followed by 2200 feet (671 meters) of test section and an additional 200 feet (61 meters) of quiescent water. The test section of the canal has a trapezoidal cross-section with a 5 foot (1.5 meters) base, a 15 foot (4.6 meters) top, and a 5 foot (1.5 meters) altitude and a bottom slope of 0.00024. The quiescent section was widened to approximate a 20 foot (6.1 meters) wide by 5 foot (1.5 meters) deep rectangular cross-section. A second weir with an optional overflow or overflow or underflow gate was installed to control flow in this section. After passage through the second weir, the water is released to a sandy basin in the adjoining desert.

Since the integrity of the original cement lining was breached by various plant forms, temporary linings were installed in portions of the canal for the present program to prevent seepage. The reservoir was lined with sheets of heavy duty polyethylene sheeting sealed together and covered with soil and gravel to prevent wind damage. The test section was treated with a slurry of bentonite clay to seal off major infiltration routes. The quiescent section of the facility was overlaid with a single fused sheet of 30 mil(0.08 centimeters) polyvinyl chloride.

During actual field studies, the flow was controlled by combining the reservoir water with the pump discharge. Total flows of 0-16 cfs (453 liters) were achieved. Flow characteristics

for the canal are illustrated in Figure 1. Run time relations are presented in Figure 2. Actual flow rates during test runs were determined both by depth sticks in the run stretch and a V notch weir. A schematic diagram of the test facility appears in Figure 3. Figures 4 through 7 illustrate the various features of the canal.

A collection boom was constructed in the quiescent section for retrieval of the floating media and porous bags. The boom was formed by sections of 2 x 4's strung on a nylon rope. A plastic skirt was attached to each segment such that it extended three inches (7.6 centimeters) into the water and three inches (7.6 centimeters) above. When buoyant carbon was employed, media was pumped from the front of the boom with a gasoline operated diaphragm pump. The collection port was funnel-shaped and sat just below the water surface in front of the boom. Holding tanks were maintained for drying and weighing the retrieved buoyant media. All porous bags were collected by hand and returned to the laboratory for regeneration.

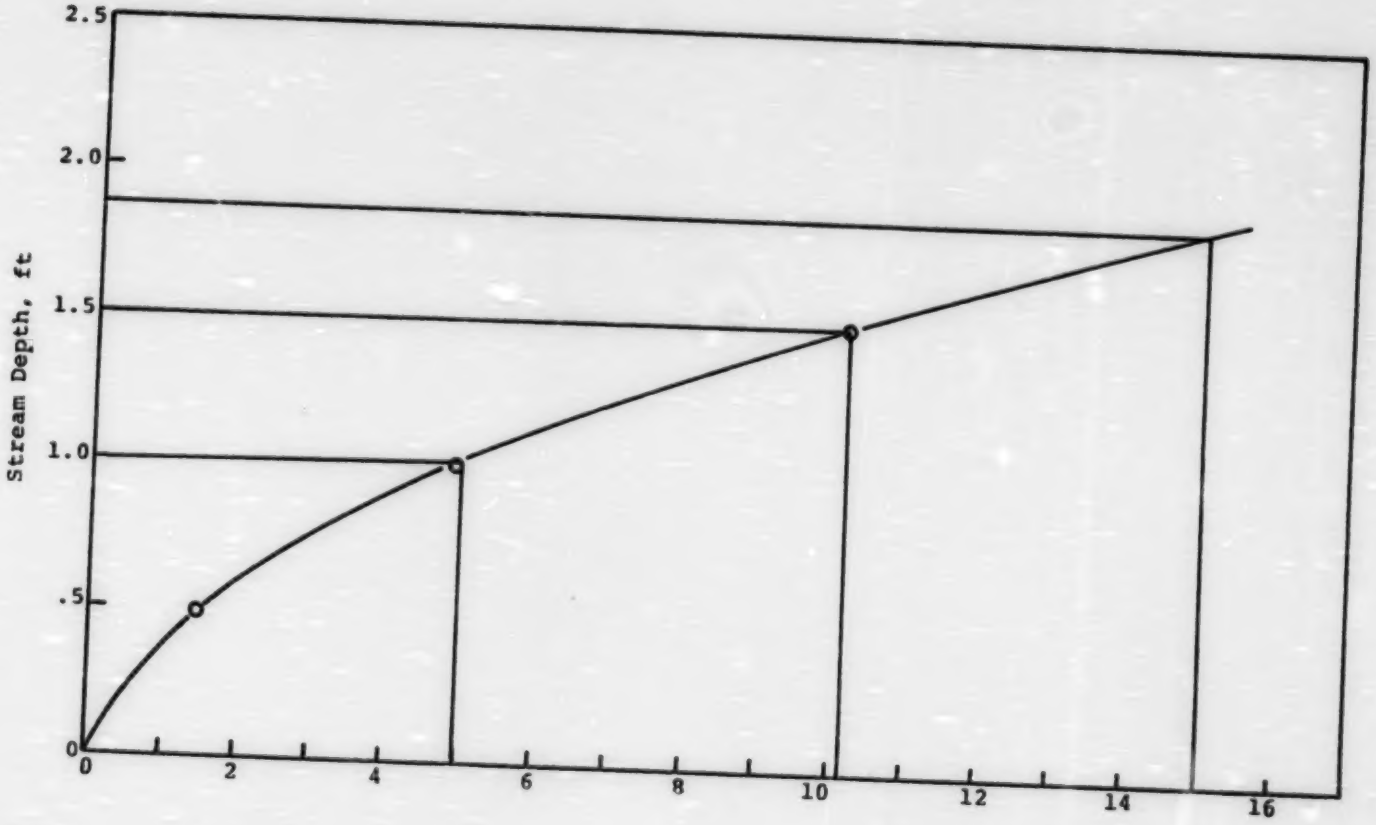

FIGURE 1. MAXIMUM STREAM FLOW RATE FOR A GIVEN STREAM DEPTH

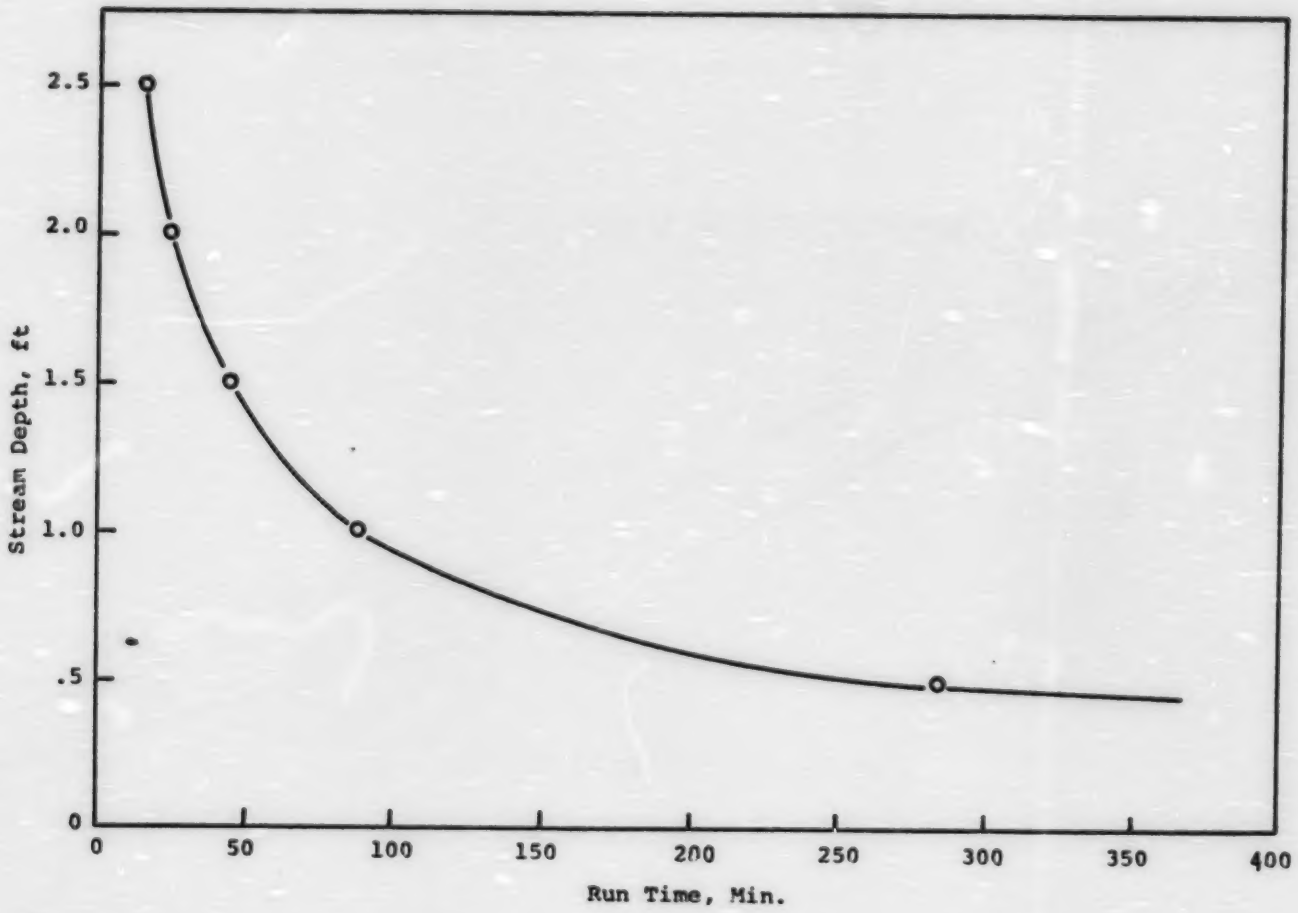

FIGURE 2. MAXIMUM RUN TIME AVAILABLE TO MAINTAIN A GIVEN STREAM DEPTH

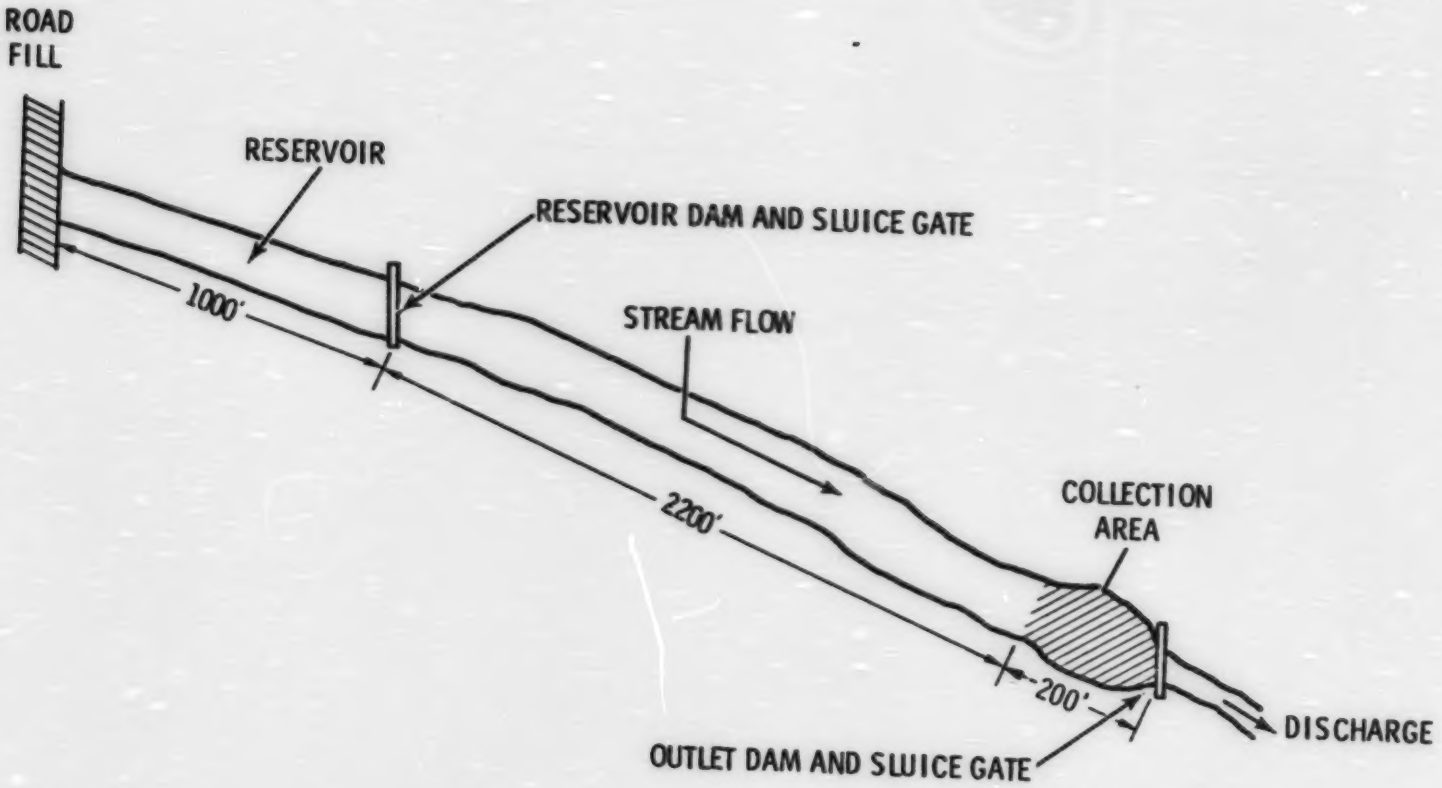

FIGURE 3. TEST SECTION OF CANAL

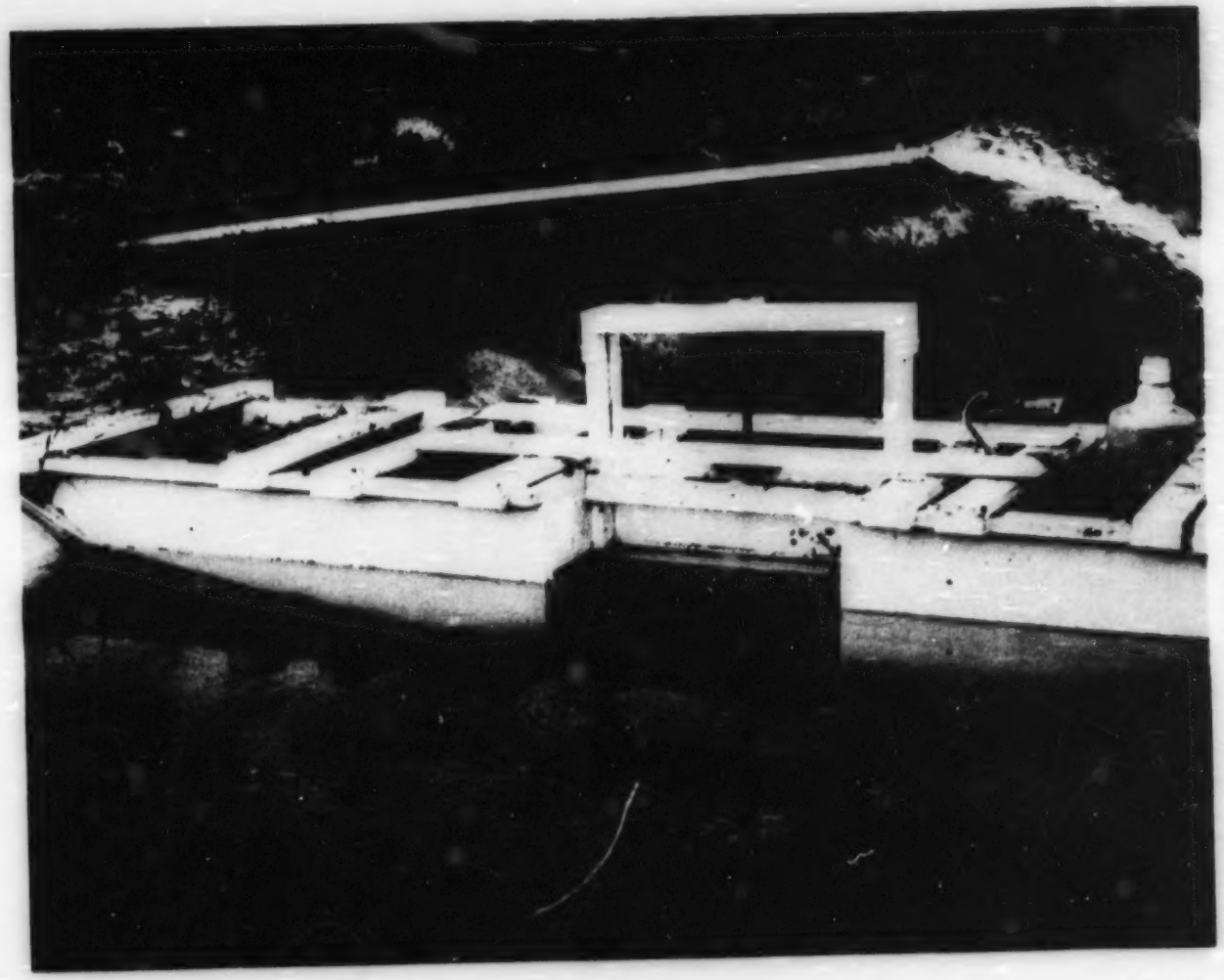

FIGURE 4. RESERVOIR SECTION OF FLOWING STREAM TEST FACILITY (FSTF) LOOKING DOWNSTREAM

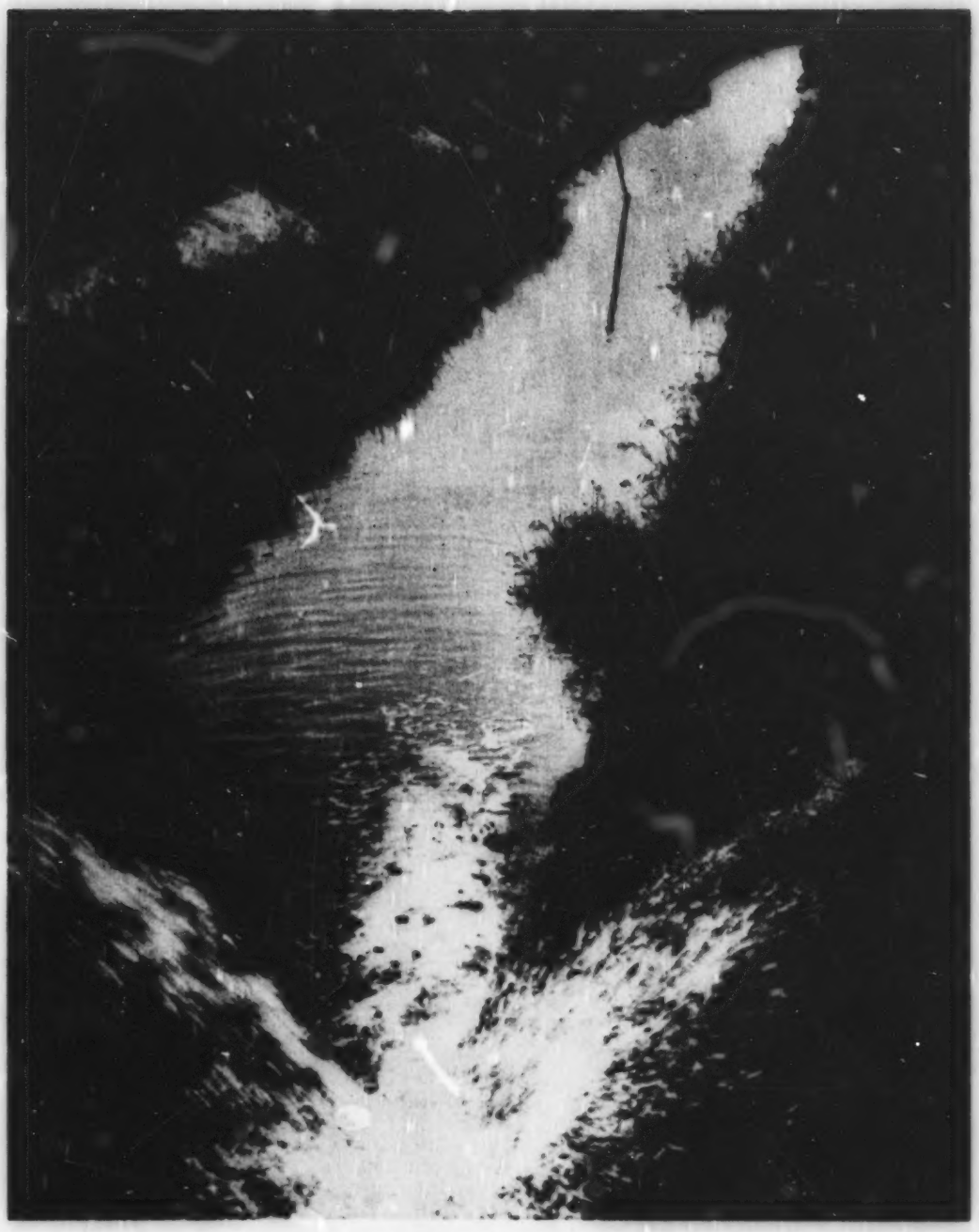

FIGURE 5. TEST SECTION OF FSTF LOOKING DOWNSTREAM

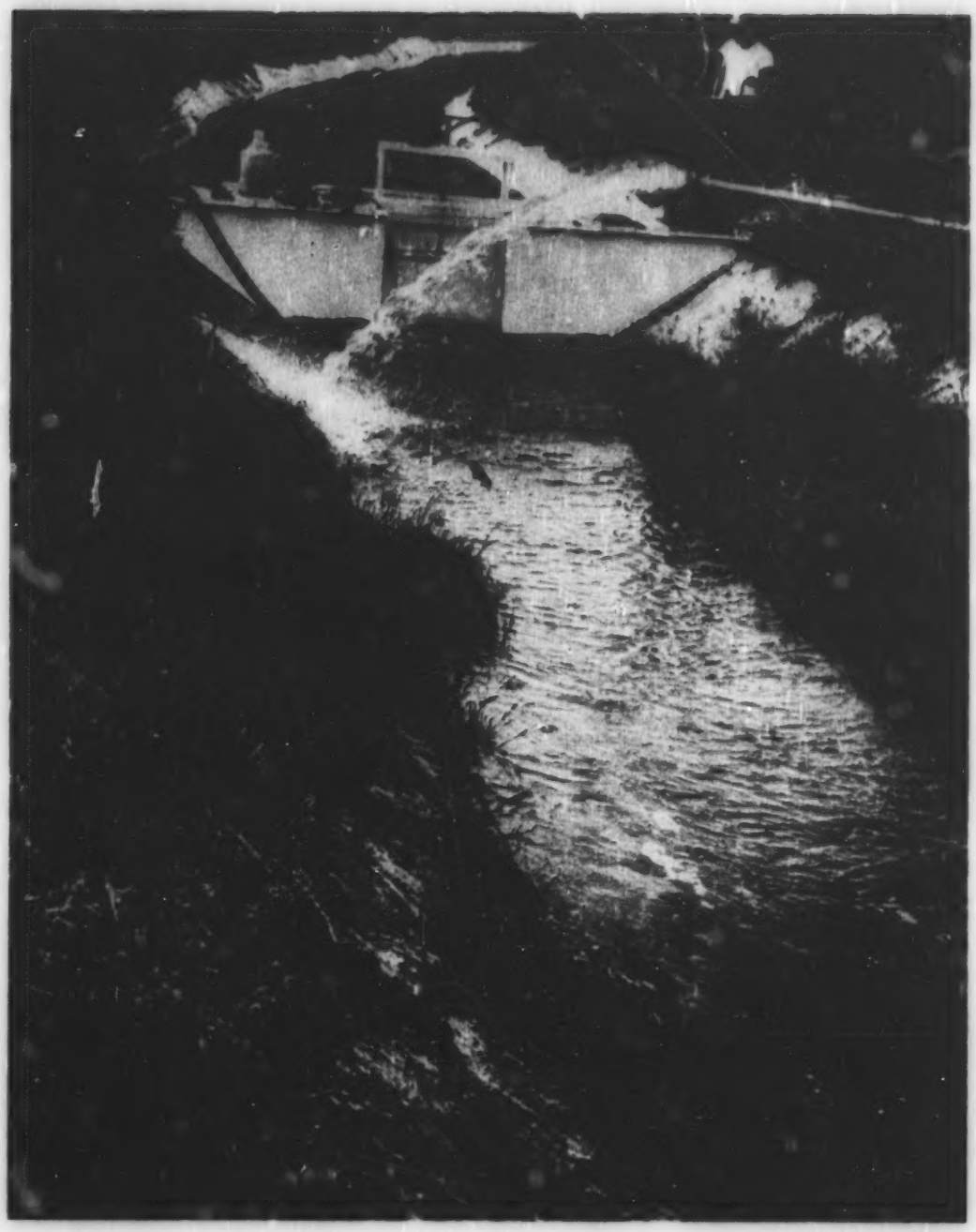

FIGURE 6. TEST SECTION OF FSTF LOOKING UPSTREAM TOWARDS RESERVOIR

FIGURE 7. QUIESCENT SECTION OF FSTF LOOKING DOWNSTREAM

SECTION 5

DESCRIPTION OF TREATMENT CONCEPTS

BUOYANT CARBON

Major problems are associated with the application of packaged buoyant media for flowing streams. As a result of movement of the contaminated plume with the current, timing of media release becomes critical. If media were delivered in packages, the release of the media from the packages would have to be timed exactly to coincide with the passage of the plume in order to achieve effective treatment. In order to avoid this problem, two alternative methods of application were explored: 1) surface application of the media with contact dependent upon the natural turnover of the stream water, and 2) subsurface injection of slurried media.

Surface application relies on two mechanisms to provide intimate contact between the contaminated water and the buoyant sorption media. Both of these are related to the natural turnover of the water as it flows downstream. The first mechanism involves the vertical velocity components of the flow itself which disperse fine media particles downward where they contact contaminated waters and sorb the contaminant. In the case of the second mechanism, the larger particles float on the surface and sorb contaminant from the deeper waters as the latter comes to the surface and rolls back to the bottom. The two mechanisms are conceptualized in Figure 8.

With subsurface application, the media is slurried and pumped into the deeper portions of the contaminant plume. Intimate contact is achieved initially through the dispersion of the slurry itself in the receiving waters and its subsequent ascent to the surface.

Optimal particle size will depend in part on the mode of application anticipated. Since surface collection of spent media in quiescent reaches is the mode of retrieval, particles must be sufficiently buoyant (a function of particle diameter when density is held constant) to rise to the surface during residence in the selected quiescent zone. On the other hand, if particles are too large they will not be carried down into the water column or will rise too quickly after subsurface injection to achieve the required contact. These system requirements, therefore, determine

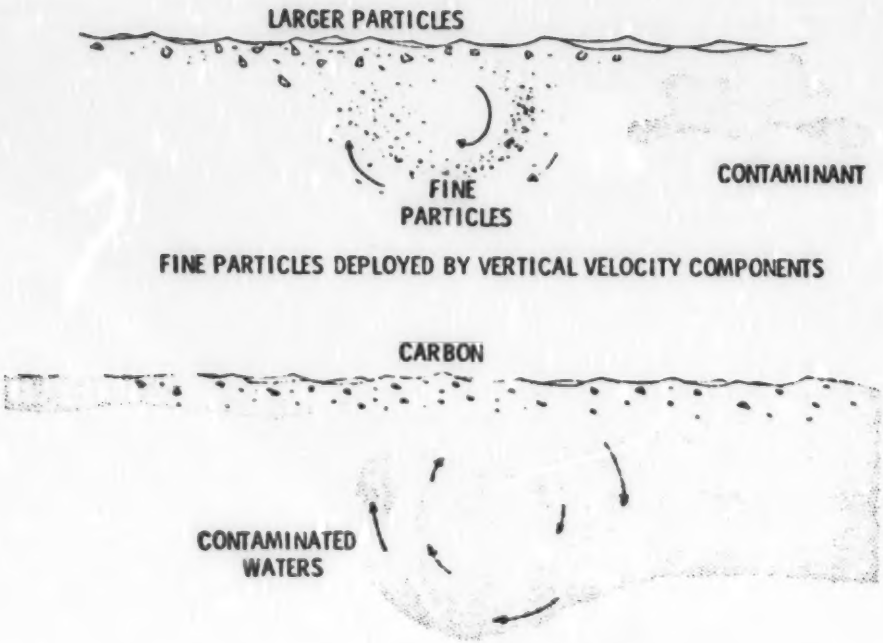

FIGURE 8. MECHANISMS FOR REMOVAL OF CONTAMINANTS BY SURFACE APPLIED FLOATING ACTIVATED CARBON

physical limitations on the acceptable particle-size range for buoyant sorption media. They, in turn, are influenced by the velocity components of the receiving waters.

Field studies were conducted to determine the approximate mesh ranges of Nuchar C-190 which would rise to the surface when applied to flowing streams. All samples greater than 250 mesh were found to be sufficiently buoyant to be recovered in quiet waters. The breakpoint for large particle sizes was more difficult to define. Whereas carbon in the size range greater than 50 mesh was found to stay on the surface with no mixing under calm conditions, a slight wind was sufficient to ripple the surface and initiate movement of the particles into the water column. To facilitate testing, selection was oriented to assure all particles could be recovered on the surface and many would mix under varying environmental conditions. For practical purposes, the optimal working range was defined as 50 x 250 mesh. While this includes many large particles which may never mix to a significant degree, it will be far less costly to obtain commercially than a narrow size range.

SINKING CARBON

The use of sinking activated carbon for in situ treatment of waters requires removal of the spent carbon from the bottom of the watercourse, abandonment of the spent media at the bottom, or incorporation of the carbon in a package which allows retrieval at some later time. The latter approach (packaging) is the most practical and was selected for development here. Each package must be designed to allow contact with contaminated water without releasing media. These requirements are similar to those which have led to the development of tea bags. Indeed, the tea bag concept is very appropriate for application of activated carbon.

Activated carbon is placed in a porous fiber bag with a preselected thread count just sufficient to hold the smallest granule sizes to be used. Contaminated water can thereby flow into the bag, contact the carbon, and flow out. As noted earlier, the bags do not perform well in static water because of a lack of flow through the bag and media. In flowing streams, however, the natural turbulence should be sufficient to constantly exchange waters in immediate contact with the bag. Contact is further stimulated by filling the bags only partially full and thereby leaving ample room for the media to fluidize. In this expanded state, adsorption kinetics are enhanced.

Adsorption will be greatly affected by carbon particle size as well as the aforementioned factors related to water exchange. The finer the particles employed, the greater the ease of fluidization and surface contact, and the more rapid the adsorption. Fine particles, on the other hand, require fine

materials to contain them which, in turn, discourages water flow. In balancing these interests, researchers at Calspan Corporation determined that commercially available granular carbons were adequate.[6] These are marketed in two size ranges: 8 x 30 mesh and 12 x 40 mesh. Early investigations were conducted with the larger carbon. The smaller 12 x 40 mesh material was selected for use in flowing streams to enhance contact with the water.

Retrieval of the "bags" can be provided for by attaching them to floats or other bouyant devices. Visual observation of the floats allows constant knowledge of where and how the bags are moving. At the end of the contact period, bags can be retrieved by placing a boom or other collection device across the channel such that the floats are snared and held against the current. Since the floats allow the bags to move with the current, the carbon is kept in constant contact with the contaminant plume. Thus, contact times can be made as long or as short as desired depending upon where collection booms are deployed. A final degree of treatment is also provided at the boom where the snared bags are analogous to a fixed carbon bed through which the contaminated water must flow.

SECTION 6

FIELD APPLICATION STUDIES WITH BUOYANT CARBON

GENERAL INFORMATION

Field studies were conducted in the Flowing Stream Test Facility at flow rates ranging from 3.98 to 4.45 cfs (113 to 126 liters). Spills were simulated with a solution of 1816 grams (4 lbs) methylisobutyl ketone (hexone), 550 grams (1 lb) of methanol, and 45 grams (0.1 lbs) of rhodamine dye. The methanol was employed as a bridge solvent to enhance the solubility of the dye and the hexone. The dye was included to allow visual monitoring of the spill plume and hence facilitate the timing of media application. Data and isotherms for the adsorption of this solution on buoyant carbon and porous bags are given in Section 8.

Three series of tests, each composed of multiple runs, were carried out during the course of the program. Each series differed in the manner in which the spill was simulated and in which the contaminant plume was allowed to develop prior to treatment. Nuchar C-190 carbon was used in all tests with carbon mesh size varied for certain of the test series. For each series of tests, a spill was conducted without application of floating media to establish background levels for the contaminant plume and the effects of natural dilution. This was necessary because, in addition to dilution, sorption onto plants and material in the test canal occurred during the course of the study. Removal was then defined as the difference between concentrations for treated and untreated samples taken at the same location.

Three sets of samples were taken during the trials. Samples were taken across the entire width of the stream at a depth of six inches (15 cm) with some provision for a larger sample input at the deeper center portion of the flow. All samples were stored in glass bottles and refrigerated until analysis. The first, at sample site S, was taken just upstream of the carbon application site. The second, at sample site C, was taken at the head end of the quiescent reach (approximately 15-25 minutes of carbon contact time). Sample site D was located at the lower end of the quiescent reach just behind the carbon collection boom. Samples at this site may not be completely representative since the 20-foot channel width and unpredictable currents make it difficult to obtain composite samples. A schematic diagram

showing the locations of the sampling points is presented in Figure 9. Three analytical techniques were initially employed to characterize the spill. Dye content was measured using a GK Turner Model 111 fluorometer. Total organic carbon content was monitored through use of a Beckman Model 915 total organic carbon analyzer. Hexone measurements were made with a Perkin-Elmer 900 gas chromatograph.

SERIES I

For the first series of tests, the hexone solution was spilled over a ten-second period at a point 200 feet (61 meters) downstream of the reservoir. This location was selected to assure that all artificial turbulence from the sluice gate was damped. Forty pounds (18.1 kilograms) of floating carbon was applied to the stream at a point 230 yards (210 meters) from the reservoir (approximately 10 minutes' flow time). Large grain size (12 x 40 mesh) Nuchar C-190 was employed for all tests. Runs involving both surface (Run 2) and subsurface (Run 3) application were conducted in this series. Surface application consisted of sprinkling the carbon on the water as the contaminant plume reached the application point. For the subsurface application case, a carbon slurry of approximately 10 g/l was prepared prior to the spill and was then pumped to the bottom of the stream as the contaminant plume passed.

Series I - Results and Discussion

Results of hexone, rhodamine dye, and total organic carbon analyses are presented in Table 1. The total material figures were derived from concentration measurements taken at specified time intervals as the plume passed the sampling point and summed for the plume at the flow rate noted.

The apparent fractions remaining in Runs 2 and 3 as compared to the blank Run 1 are given in Table 2. Table 3 shows the apparent fractions remaining when compared to the initial samples at site S. Several observations are in order.

It is evident from the data that a large fraction of the hexone cannot be accounted for. Only 26 to 34 percent of the original 1816 grams (4 lbs) of hexone was detected in the initial, untreated S samples. Similarly, only 39 to 45 percent of the original TOC was detected at site S, while virtually all of the dye was accounted for. The data suggest that the apparent loss in TOC can be attributed almost entirely to the apparent hexone loss. At site S, the loss in hexone, 1200 to 1535 grams (2.6 to 3.3 lbs), translates into a theoretical TOC loss of 864 to 1052 grams (1.9 to 2.3 lbs) as compared to a measured TOC loss of 826 to 926 grams (1.8 to 2 lbs).

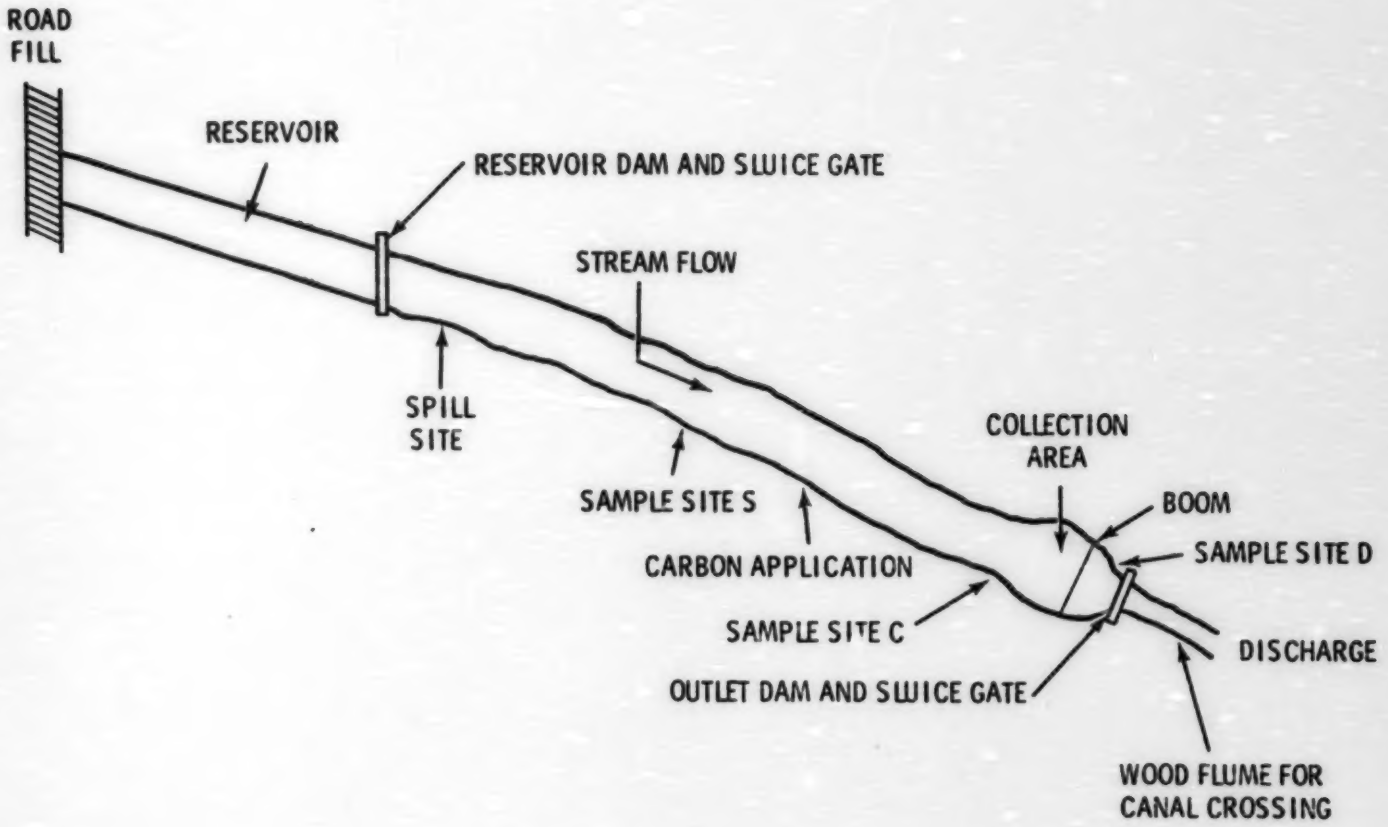

FIGURE 9. SAMPLING SITE LOCATIONS FOR TEST SERIES #1

TABLE 1

ANALYSIS OF SERIES OF #1 SPILL PLUMES

	Run #1 Blank 6761 l/min (3.98 cfs)	Run #2 Subsurface Slurry Application 9173 l/min (4.45 cfs)	Run #3 Surface Application 9173 l/min (4.45 cfs)
Sample Site S			
Total Hexone (g)	616	481	589
Total Organic Carbon (g)	687	591	587
Total Dye (g)	44.0	38.1	34.9
Sample Site C			
Total Hexone (g)	670	643	508
Total Organic Carbon (g)	872	559	751
Total Dye (g)	37	10.0	1.5
Sample Site D			
Total Hexone (g)	752	223	341
Total Organic Carbon (g)	737	271	574
Total Dye (g)	26.7	1.4	0.76

TABLE 2

TEST SERIES # 1
APPARENT FRACTION REMAINING COMPARED TO BLANK RUN # 1

	Run # 1	Run # 2	Run # 3
Sample Site S			
Hexone	1.00	.78	.95
Organic Carbon	1.00	.86	.86
Dye	1.00	.86	.79
Sample Site C			
Hexone	1.00	.96	.76
Organic Carbon	1.00	.64	.86
Dye	1.00	.27	.04
Sample Site D			
Hexone	1.00	.30	.45
Organic Carbon	1.00	.37	.78
Dye	1.00	.05	.02

TABLE 3

TEST SERIES # 1
APPARENT FRACTION REMAINING COMPARED TO INITIAL SAMPLE S

	Run # 1	Run # 2	Run # 3
Sample S			
Hexone	1.00	1.00	1.00
Organic Carbon	1.00	1.00	1.00
Dye	1.00	1.00	1.00
Sample C			
Hexone	1.08	1.34	.86
Organic Carbon	1.27	.94	1.28
Dye	.84	.26	.04
Sample D			
Hexone	1.22	.46	.58
Organic Carbon	1.07	.46	.76
Dye	.61	.04	.02

Since methanol is more volatile than hexone and apparently little methanol is unaccounted for, evaporation does not appear to be a plausible explanation of the apparent loss. A more reasonable explanation is that the dye and the methanol are both water soluble to a greater extent than hexone and hence can be expected to be selectively extracted from the hexone into the water. The hexone would then form a lighter floating layer of hexone and hexone-saturated water solution which would mix more slowly with the remaining water column. There would then be a gradient from high hexone concentrations at the surface to lower concentrations with depth below the surface. Hence, samples taken at a six-inch (15 cm) depth may underestimate hexone content considerably. This incomplete mixing hypothesis would also explain the apparent production of hexone in the blank run as the plume moved downstream. That is, with movement downstream, turnover and vertical dispersive forces would slowly bring the hexone to an isoconcentration state thus making the amount of hexone at the six-inch depth level more representative. This would be especially true of the site D samples since it is downstream of the containment boom which would stimulate vertical currents.

Stratification of this nature could well affect removal efficiency. Whereas the apparent removals were 64 and 45 percent hexone, respectively, more than half of the original spill was on the surface of the flow where the bulk of the carbon remained. Hence, all of the missing hexone may well have been sorbed on the carbon by the end of the run. Removal of dye was consistently better than 90 percent. This does not allow for corrections required as a result of differences in absorption onto plants and soil in the treated runs as compared to the blank run, but there is no reason to believe such a correction would be very large.

There appears to be no advantage to use of slurry application over surface application with the larger grain size carbon. This may in part be an artifact of the mode in which the slurry was pumped into the ditch, but more likely it reflects the quick rise time for the large particles and hence a minimal amount of increased contact with submerged waters. The advantages of subsurface injection are likely to become apparent in deeper streams where surface application leads to contact with only a portion of the contaminated plume.

Comparison of TOC, hexone, and dye levels reveals no constant relation between any two parameters. This might be expected since the three components vary in their solubility, tendency to stratify, and adsorptive properties. The use of gas chromatography for hexone detection proved very satisfactory with good reproducibility on field samples and standards. Therefore, since hexone was the major component of the spill, hexone analysis was selected as the major measurement basis in subsequent trials. TOC and dye measurements were used sparingly to provide confirmation on hexone data.

During the first series of runs, several environmental factors were found to complicate spill response activities. It was found that wind conditions greatly influenced the effective contact time achieved during any single run. The larger, more buoyant carbon particles stayed at, or very near, the surface throughout the test period. Wind moving in the direction of the flow accelerated the floating media to a velocity much greater than that of the spill plume itself. Thus, after a short contact period, the carbon passed the contaminant plume and moved downstream in contact with relatively unaffected waters. Under calm conditions, a similar development was observed to occur over a longer period of time as a result of the greater relative velocity of the surface waters to that of the deeper layers. Conversely, when winds prevailed in a direction counter to flow, the carbon stayed with the contaminant plume throughout the test period.

Difficulties were also experienced in collecting the spent carbon. The carbon was easily detained behind a wooden boom fitted with plastic skirts. When an attempt was made to pump the contained carbon to a holding facility, however, it was found that abundant plant debris quickly plugged the lines. The debris was excessive as a result of the intermittent flow pattern in the test facility. During dry periods, various wind-blown plant forms accumulated in the run stretch. Initiation of flow then scoured these weeds throughout the 2 to 3 hour test period. This should not prove to be a major problem in natural streams if flooding is not occurring. Additionally, coarse screens preceding the intake line were found to remove most of the plant debris and thus enable collection of the carbon.

SERIES II

For the second series, the dye-hexone-methanol solution was added to the turbulent waters at the foot of the reservoir weir with a variable speed pump over a five-minute time period. The pumping rate was adjusted to simulate the concentration gradient observed in well-developed plumes. Carbon addition was carried out at a distance 50 yards (45.7 meters) downstream from the simulated spill. Hence, carbon contact time prior to booming in this series of runs was 50 percent longer than in previously reported runs. The locations of the application point and sampling sites are indicated in Figure 10.

Series II - Results and Discussion

Results of runs conducted in this manner are presented in Table 4. The coarse carbon employed was the standard 12 x 40 mesh Nuchar C-190 applied in previous tests. The fine carbon was 60 x 230 mesh Nuchar C-190. The latter was produced by first grinding the commercial carbon and then sieving it to specifications. Each test involved the use of forty pounds of carbon and four pounds of hexone as in previous trials.

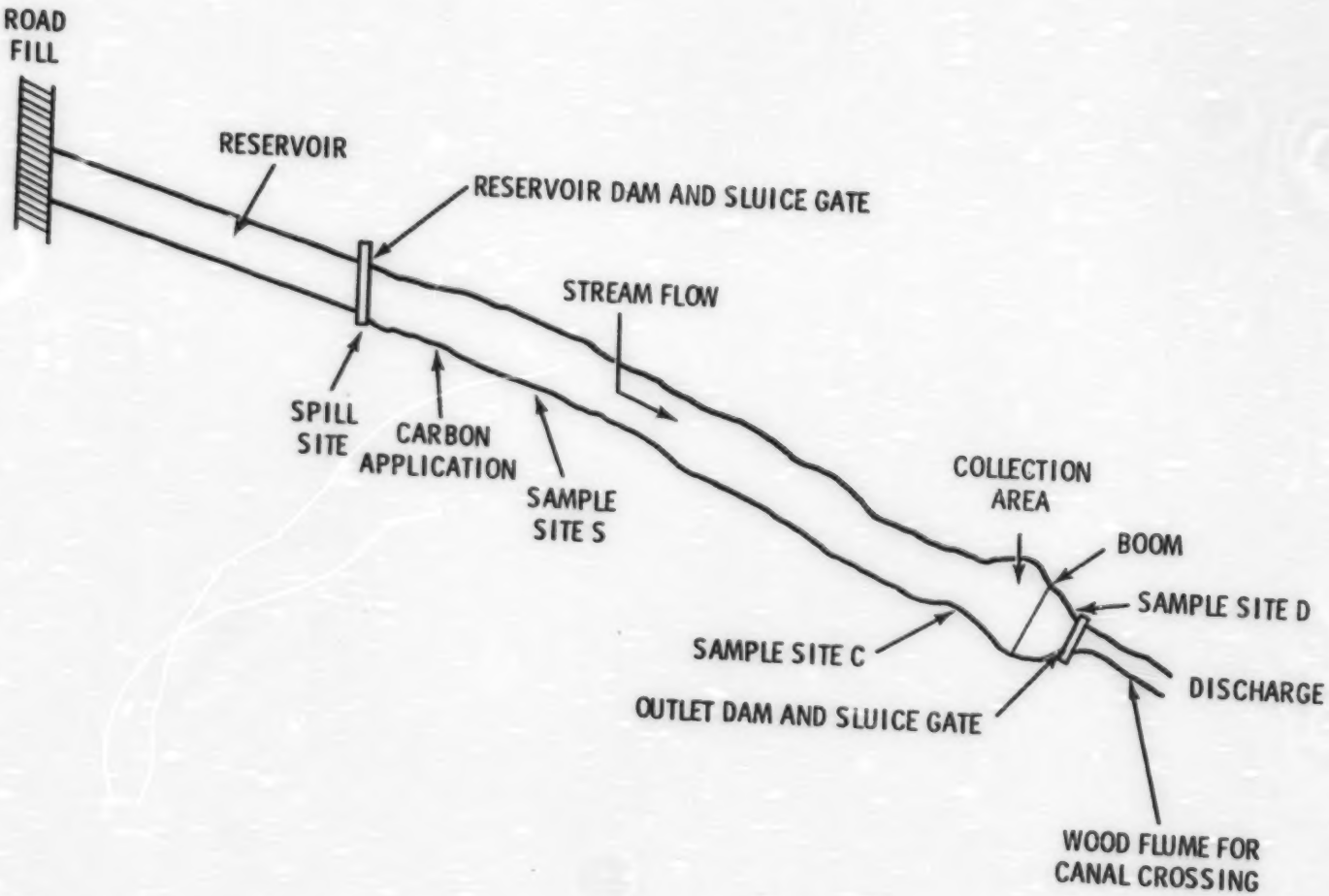

FIGURE 10. SAMPLING SITE LOCATIONS FOR TEST SERIES #2 AND #3

TABLE 4

TEST SERIES #2
RESULTS OF RUNS WITH SPILLS IN TURBULENT SECTION OF THE FLOWING REACH

Run No.	Description of Run	Hexone at Sample Site S (total g)	Percent Remaining Run/ Background	Hexone at Sample Site C (total g)	Percent Remaining Run/ Background	Hexone at Sample Site D (total g)	Percent Remaining Run/ Background	Hexone on Carbon (total g)	Percent Hexone Accounted for at Site D Total/1816 g
1	Background	1986	100	1650	100	1408	100	--	78.0
2	Slurry Addition of Coarse Carbon	1618	81	1222	74	1592	113	219	99.7
3	Surface Addition of Coarse Carbon	925	47	1186	72	1242	88	162	77.3
4	Surface Addition of Fine Carbon	987	50	1201	73	1170	83	185	74.6

From the data of Table 4, it can be seen that subsurface slurry addition of the coarse carbon was not as efficient as surface application of the coarse or fine carbons. The fine carbon effected a better overall removal than the coarse carbon. It is interesting to note that removal declined with travel down the canal. This is thought to be a result of desorption as loaded carbon traveled past the contaminant plume and became exposed to "uncontaminated" waters. Subsequent work in the laboratory revealed that desorption does indeed occur. This will not be the case with all hazardous substances since some have very shallow sorption isotherm slopes, and others undergo irreversible adsorption.

Desorption apparently did not occur in prior runs because of the shorter distance traveled and the stratification of the hexone. Had the last test series been terminated at sample point S, removal would have been comparable with that reported for the prior runs. It is also interesting to note that much more hexone is accounted for at all sample sites than in test series 1 or 3. This further substantiates that better mixing was achieved when the hexone was pumped into the water column, and therefore samples taken at depth were representative of the plume.

Samples of spent carbon were collected at sample site D. These were subsequently eluted with four methanol rinses to desorb hexone. (Previous laboratory work indicated >95 percent recovery can be achieved with a series of four methanol washes.) The methanol was then analyzed with the gas chromatograph to determine the total hexone contained in the forty pounds of carbon applied to the spill. This input then was added to the quantity measured in the water to complete a material balance on the hexone. Recovery was typically 74-78 percent except for Run 2 where an extraordinary 99.7 percent was accounted for. This figure is believed to reflect a non-representative sample of carbon.

SERIES III

The third series of runs was performed to evaluate instantaneous spill application. For this series, the dye-hexone-methanol solution was spilled instantaneously (duration ~10 seconds) at the reservoir weir. Carbon application and sample sites remained the same and can be seen in Figure 9. Forty-eight pounds (21.7 Kg) of fine carbon (60 x 230 mesh Nuchar C-190) was then spread on the surface.

Series III - Results and Discussion

Results of this application are presented in Table 5. It would appear that hexone stratification again occurred. As in test series 1, the recovery of hexone at sample site S during the

TABLE 5

TEST SERIES #3
RESULTS OF INSTANTANEOUS SPILL CONDUCTED AT RESERVOIR WEIR

Run No.	Description of Run	Hexone at Sample Site S (total g)	Percent Remaining Run/ Background	Hexone at Sample Site C (total g)	Percent Remaining Run/ Background	Hexone at Sample Site D (total g)	Percent Remaining Run/ Background	Hexone on Carbon (total g)	Percent Hexone Accounted for at Site D Σ Total/1816 g
1	Background	794	100	1364	100	1418	100	--	78
2	Forty-eight Pounds Fine Carbon Applied at Surface	714	90	1045	77	722	51	118	46

backgournd run is quite low. This suggests that it was not the turbulence at the weir that eliminated stratification in the second test series so much as the means of introducing the hexone to the water. In Series II, when the hexone was pumped into the water the discharge end of the hose was placed down into the water column. This apparently created much better mixing and minimized the effects of stratification. The removal obtained in the final test is comparable with that noted in the shorter runs of test series 1. Removal clearly is enhanced with stratification. This no doubt reflects the greater contact between the carbon and the concentrated portion of the hexone plume at the surface. The poor recovery of hexone in the material balance is similar to results obtained in test series 2.

Samples of carbon were taken at each sampling site to investigate desorption. The total hexone accounted for on the carbon was 0.02 ounces (0.67 g, 4.76 ounces (135 g), and 4.16 ounces (118 g) for sites S, C, and D, respectively. Some desorption appears to have occurred, but the effect was generally overwhelmed by the effects of stratification. Desorption in this case may be the result of either passage back into the water column or volatilization to the atmosphere. Some degree of the latter would tend to explain the poor material balance results. The potential for volatilization from the carbon is greater than that from the water itself since the black carbon absorbs a great deal of solar radiation and thus heats the hexone directly. In this respect, the carbon may act as a wick withdrawing hexone from the water and releasing it to the atmosphere.

During the various test runs, it was noted that carbon loss along the sides of the stream was not significant. Carbon recovery with the booming system, on the other hand, was very effective with in excess of 90 percent of both the fine and the coarse carbon accounted for. The degree to which simple booms can hold and direct floating carbon movement is illustrated in Figure 11.

EFFECTIVENESS OF CARBON CONTAINMENT BOOM

An independent evaluation was made to determine the extent to which various size fractions of floating carbon are carried beneath the surface of the water. Seventy-five gram (2.65 ounces) samples of carbon were slurried and added to the center of the stream flowing at 5 cfs (141.6 liters) in the run stretch of the FTFS. A skimming device was then employed to collect all carbon found in the top 0.5 inches (1.3 cm) of water some 25 feet (7.6 meters) downstream. Results are presented in Table 6. All size fractions tested appear to be capable of mixing below the surface in this section of the facility. The ratio of surface residuals shows significant differences in this parameter.

Based on this preliminary work, test conditions were selected for the parallel evaluations between floating carbon

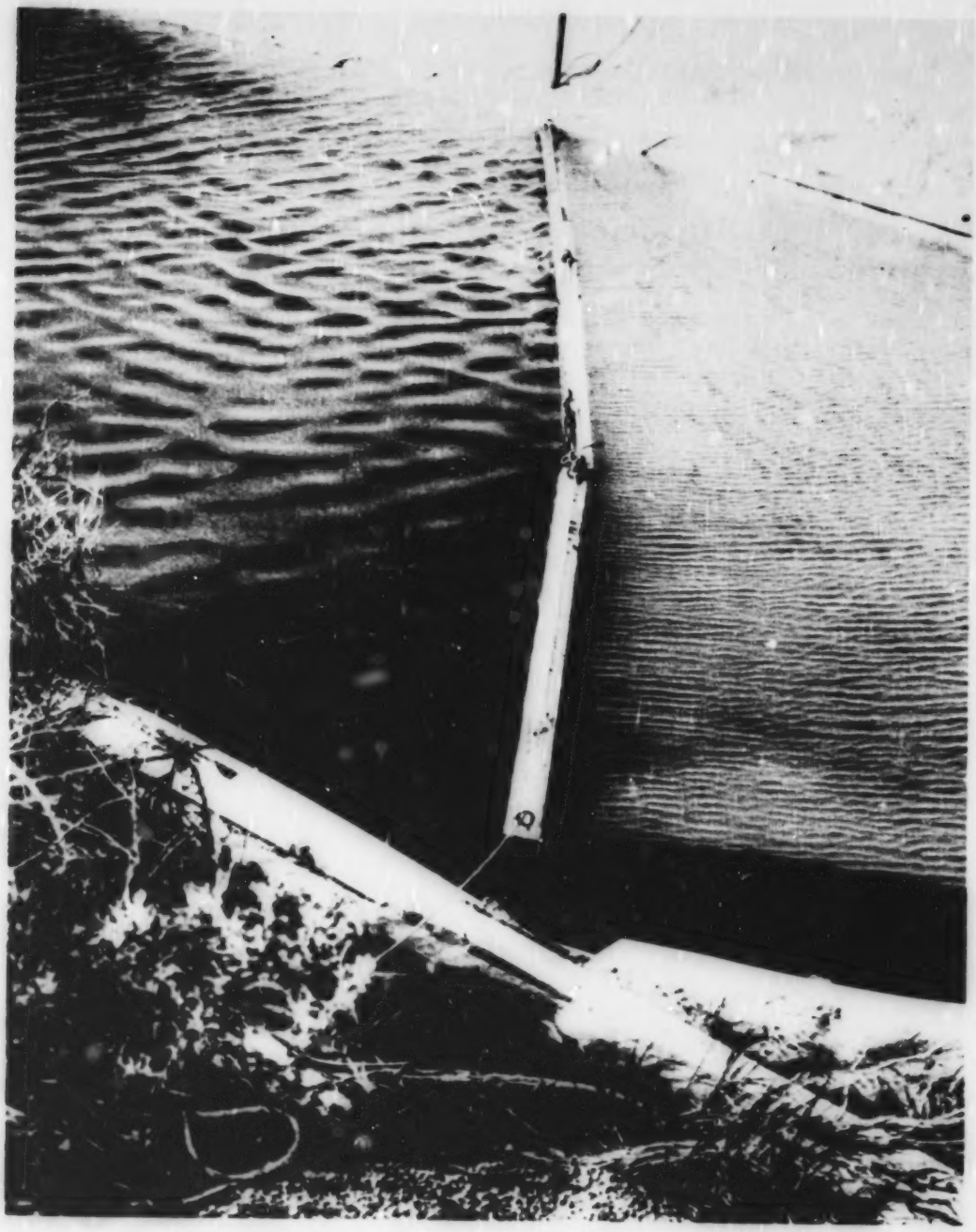

FIGURE 11. BOOMING FLOATING CARBON IN QUIESCENT SECTION OF FSTF

TABLE 6

RECOVERY OF VARIOUS SIZED PARTICLES FROM APPLICATION OF 75 GRAMS OF FLOATING CARBON

Mesh Range	40x60	60x70	70x100	100x200	200x325
Total Wt. Recovered	1.6954	1.4215	0.6308	0.2356	0.1615
Percent of Sample Applied	2.26	1.90	0.84	0.31	0.22
Ratio*	1.00	0.838	0.372	0.139	0.095

*Ratio of weight recovered to weight of 40x60 mesh sample recovered

and sinking carbon in porous bags. The spill application employed in test series #3, instantaneous spillage at the tail race, was deemed the most advantageous for further testing. It simulates actual spill conditions most closely, and minimizes variations between tests which might result from attempts to pump the hexone into the canal in a simulated plume. At the same time, the flow pattern at the tail race spreads the plume out analogous to a dispersed plume that has had time to develop. Spills made further down the canal remained concentrated during the brief run times available.

SECTION 7

DEVELOPMENT OF THE POROUS BAG SYSTEM

Many of the important conceptual aspects of applying sinking carbon in porous bags were addressed in early work.[4,6] Therefore, preliminary efforts in this study focused on specific design considerations with respect to large scale production and application in the FSTF. These activities were divided between two objectives: bag design, and regeneration.

POROUS BAG DESIGN AND FABRICATION

While previous studies have shown that removability is largely a function of carbon mesh size, bags for use in the FSTF were designed to enhance removability by maximizing responsiveness to water currents. Original specifications called for bags to be shaped like long thin fibers with outside dimensions of 1 (2.5 cm) x 12 (30.5 cm) inches. Practical considerations, however, dictated expansion to a width of three inches which allowed greater ease in loading and larger amounts of carbon per bag.

Pursuant to the goal of minimizing absorption kinetic problems, a finer 12 x 40 mesh Filtrasorb carbon produced by Calgon Corporation was selected for field testing. This necessitated the use of a fabric with an ASTM mesh count of 51. In order to allow steam regeneration of spent bags, fabric types were sought that would withstand heat, moisture, and the hexone solvent. After review of various commercially available materials, a polyester monofilament screen cloth produced by Kressilk Products, Inc. was selected for construction of bags.

General fabrication procedures for producing the porous bags are given in Figure 12. Sheets of screen cloth were cut to 28 (71.1 cm) by 12 (30.5 cm) inches and sealed on three sides with double stitching (Step A). All stitching was accomplished with a commercial upholstery machine using heavy duty dacron thread. Vertical double stitching was then added at 3 inch (7.6 cm) intervals forming eight consecutive bags side by side (Step B). Individual bags were then separated by cutting between the double stitching (Step C). Each bag thus formed was then charged with 62 ounces (17.5 grams) of Filtrasorb (Step D). Bags were sealed with stitching and carbon spread evenly inside each (Step E). Horizontal spaces were then cleared at three inch

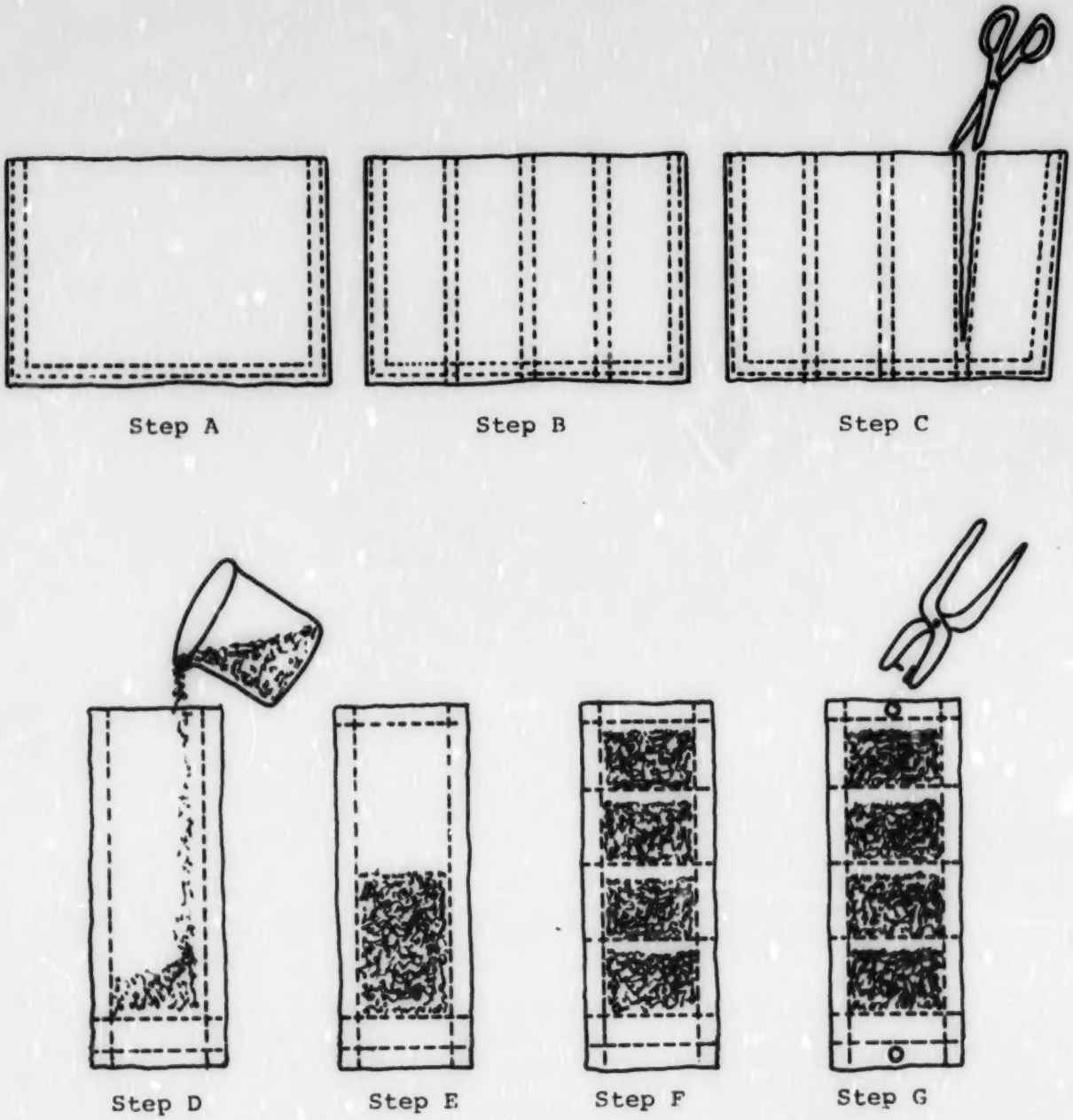

FIGURE 12. FABRICATION PROCEDURE FOR PRODUCING POROUS BAGS

intervals and stitching added to form four 3 inch (7.6 cm) squares in each bag containing equal quantities of carbon and sufficient free space to allow fluidization (Step F). Finally, grommets were affixed to the one inch margins at the top and bottom of the bags (Step G). In excess of 700 bags were produced in this manner. A typical bag appears in Figure 13.

Grommets on each bag facilitated attachment to floats and linear attachment of bags for deep waters. Wooden floats were constructed from 15 inch (38.1 cm) long 2 by 2's for the tests conducted here. Eye hooks were placed in the end of each of these and a loop of twine threaded through forming a complete circle around each float. Six bags, three each side, were then threaded onto each float. A completed float set is pictured in Figure 14.

POROUS BAG REGENERATION FACILITY

Because of the cost of producing the porous bags it was determined that carbon should be regenerated after use rather than discarded. This can be accomplished in one of two ways: 1) separation of carbon from the bags followed by regeneration, and 2) regeneration of the carbon while still in the bag. The latter involves the least amount of time and labor, but is limited in that thermal regeneration is precluded. For the purposes of the work reported here, it was determined that hexone and methanol are sufficiently volatile to be removed by steam stripping. Since the nylon fabric in the bags was guaranteed for temperatures up to 300° F (148.9° C), no separation from the bags was necessary.

A steam generation unit and contact tank were constructed for all subsequent regeneration work. A schematic of the facility is pictured in Figure 15. Spent bags of carbon were separated from the wooden floats and stacked in the stripping tank. Packing was added as needed to minimize short circuiting. Bags were then steamed over a 12 hour period.

The stripping unit was tested early in the program to assess effectiveness. The bottom square of three individual bags were suspended in beakers containing 1.7 ml hexone in one liter of water. After stirring for one hour, bags were retrieved and two units placed in the steam stripper for regeneration over a four hour period. The third bag was held out for control purposes. After regeneration, carbon samples were removed from the bags and residual hexone extracted utilizing four rinses of methanol. The extract was then analyzed by gas chromatography while the carbon was dried at 103° C (217.4° F) and weighed. Analysis indicated that 70 percent of the absorbed hexone was removed during the four hour period. Based on these results, a 12 hour exposure was selected as adequate for regenerating bags used in field trials.

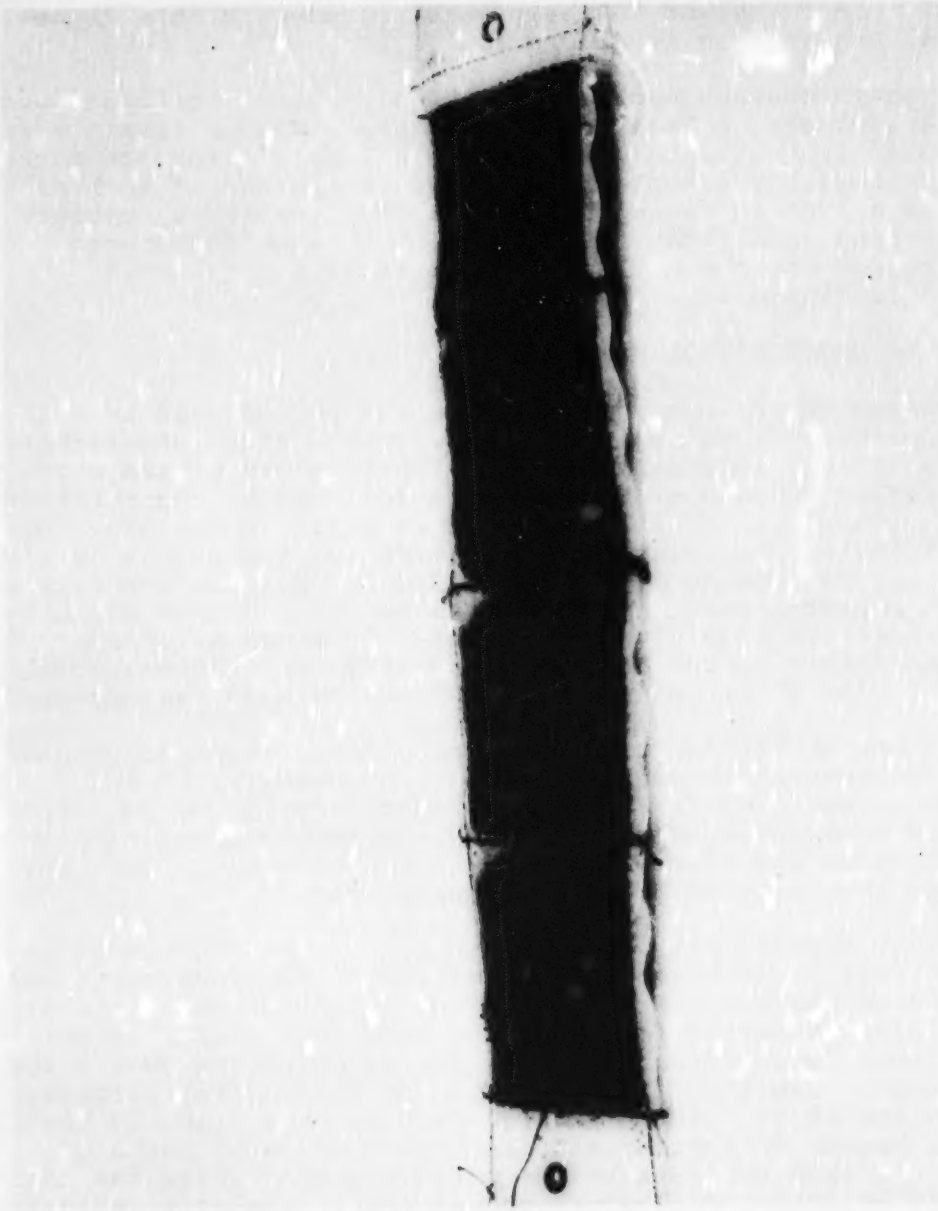

FIGURE 13. COMPLETED POROUS BAG

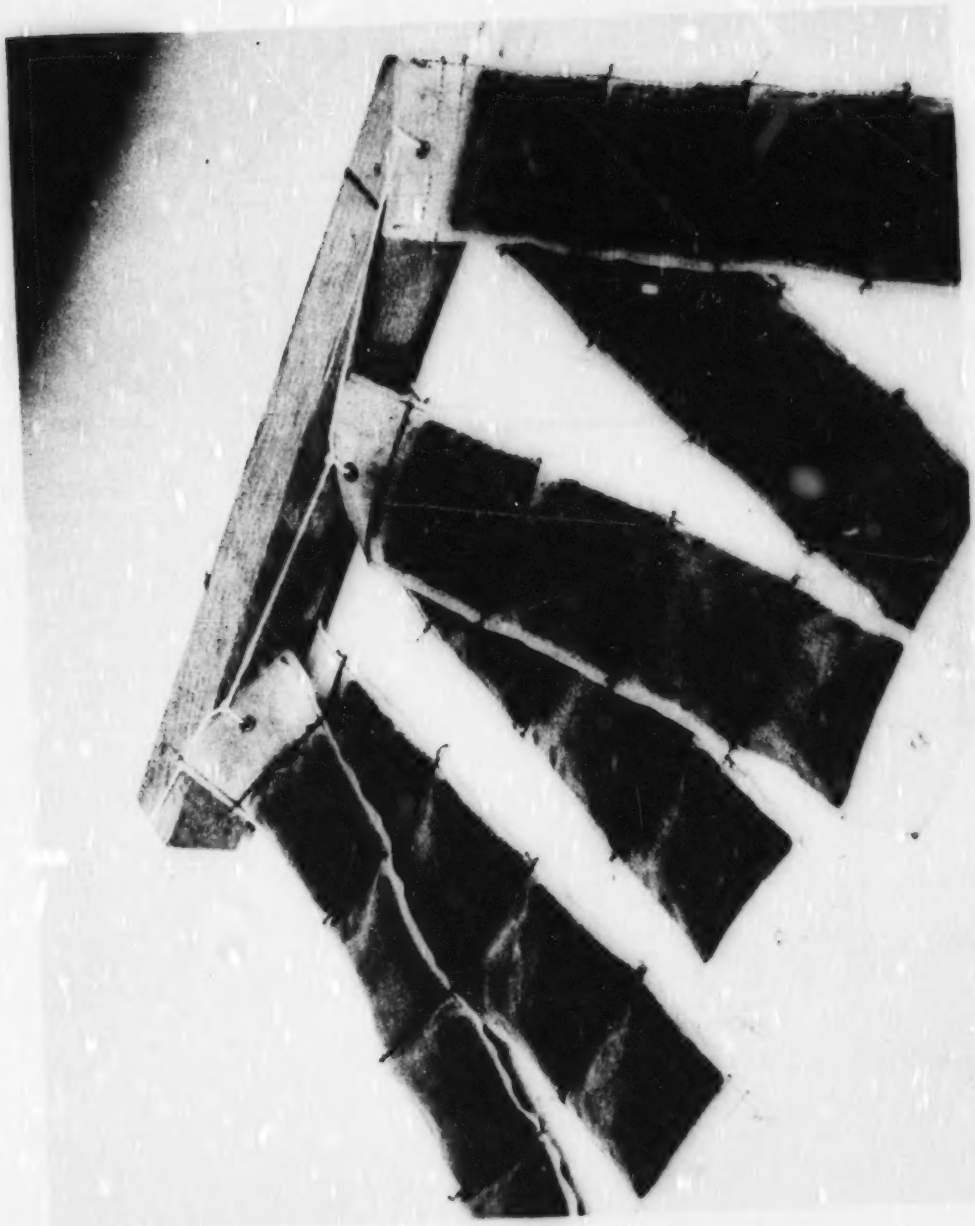

FIGURE 14. STANDARD FLOAT ARRANGEMENT

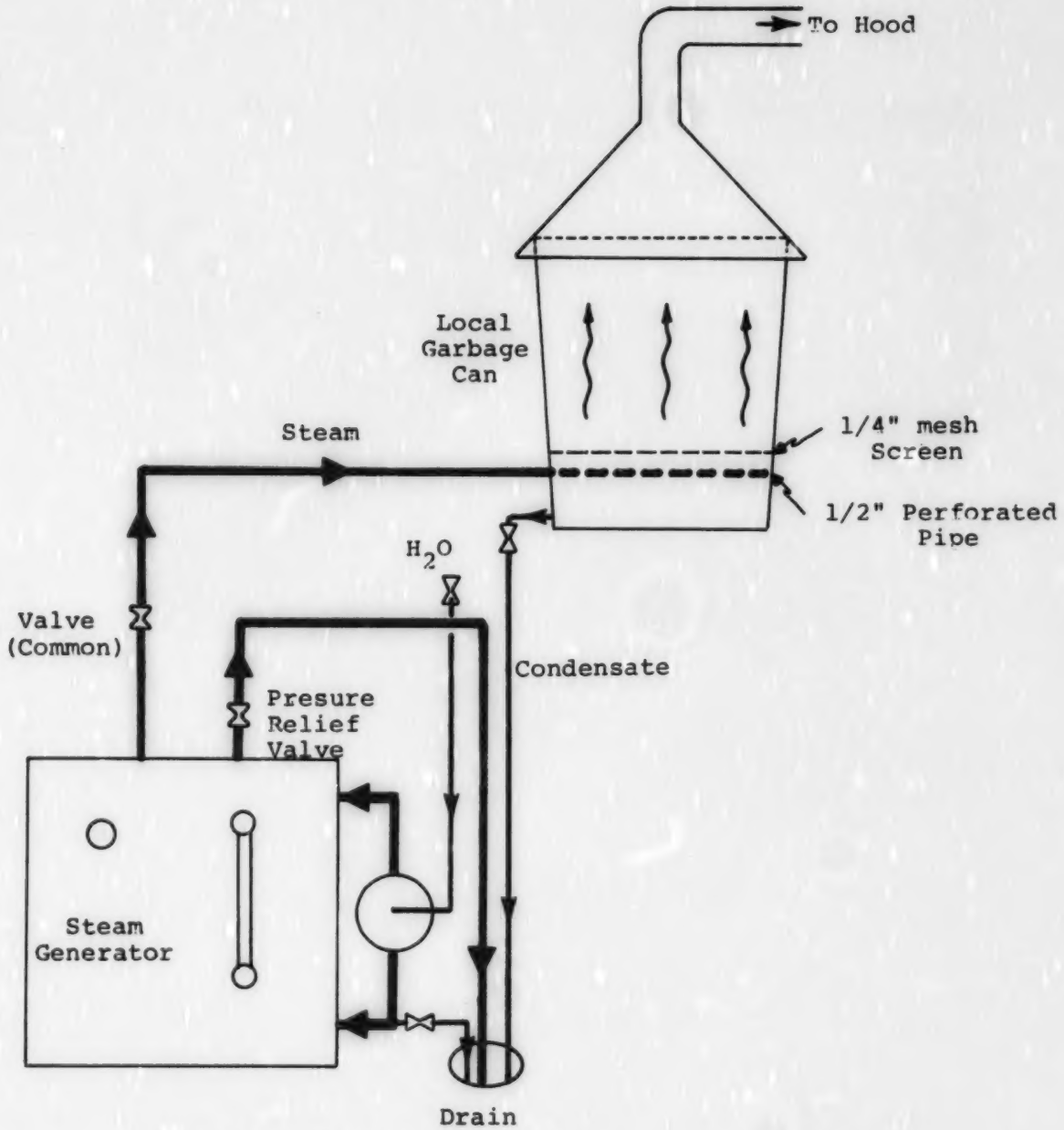

FIGURE 15. SCHEMATIC OF STEAM STRIP REGENERATION FACILITY

A preliminary run was performed on the FSTF to assure that the bag design selected was compatible with flow conditions. No problems were encountered with bags catching on obstacles on the bottom of the channel. Up to 25 percent of the floats caught on weeds or other intrusions along the shoreline during the run. Aside from this, no operational problems were noted, and subsequent studies were directed to the parallel evaluation of floating carbon and porous bags.

SECTION 8

COMPARATIVE STUDIES OF ALTERNATE CARBON SYSTEMS

As was the case for field application studies with floating carbon, all comparative evaluations were conducted in the FSTF. Sample collection and media application sites were the same as those identified in Figure 10. Tests at each flow rate were conducted in series and included one run each with the application mode to be studied and a blank background run to which no carbon was added. Hexone was spilled instantaneously at the tail race of the reservoir gate.

Buoyant carbon was wetted and air dried prior to each run. Application was made by manual distribution on the surface of the stream. Porous bags were similarly air dried prior to testing, but no wetting was deemed necessary since bags were cooled in the steam stripping tank prior to removal. Floats were manually placed in the stream for testing.

Field evaluations focused on determining the comparative performance of systems with variation of two parameters -- flow rate and spill concentration. Flow rate studies were conducted for discharges of 5 (141.6 liter), 10 (283.2 liter), and 15 (424.7 liter) cfs. Results of test runs are presented in Table 7. In general, buoyant carbon was more effective than porous bags for removing hexone at all flow rates tested. Differences in removal rates at specific flow rates were sufficiently small to suggest an origin of sampling discontinuities. Removal averaged 50 percent. The porous bags, on the other hand, displayed an increasing removal capability with higher flow rates. This implies that poor removal at low flow rates results from poor adsorption kinetics. Increased turbulence at higher flow rates apparently overcomes these difficulties. It is emphasized that this effect is related to the turbulence in the stream and not the flow rate percent. In this respect, velocities associated with these flows are a better determinant of the conditions which sponsor removal with porous bags than are the flows themselves. For the flow rates tested, average velocities were in the range 0.84 (25.6 cm)-1.17 (35.6 cm) ft/sec with greater surface velocities.

Sorption characteristics for the hexone solution on floating carbon and a porous bag are given in Figure 16. Tests were conducted in polyethylene bottles placed on a shaker for

TABLE 7

COMPARISON OF IN SITU TREATMENT EFFICIENCIES AT VARIOUS FLOW RATES

Flow Rate	Mode of Run	Hexone at Sample Site S (Total g)	Percent Remaining (Run/Bkgrd)	Hexone at Sample Site C (Total g)	Percent Remaining (Run/Bkgrd)	Hexone at Sample Site D (Total g)	Percent Remaining (Run/Bkgrd)
4.45	Background	794	.100	1,364	100	1,418	100
4.45	Floating	714	90	1,045	77	722	51
6.49	Background	665	100	2,469	100	1,344	100
6.49	Porous Bags	811	100+	1,678	68	1,916	100+
12.6	Background	1,441	100	2,265	100	2,135	100
12.6	Porous Bags	907	63	1,644	73	1,939	91
10*	Floating	2,739	100+	1,783	100+	1,201	62
15	Background	1,860	100	2,849	100	2,818	100
15	Porous Bags	2,003	100+	2,634	92	2,379	84
15	Floating	1,089	59	1,634	57	1,299	46

*Operational problems caused rapidly declining flow rate which led to overestimation of hexone remaining at each sample site. Actual removal believed to be somewhat better than reported.

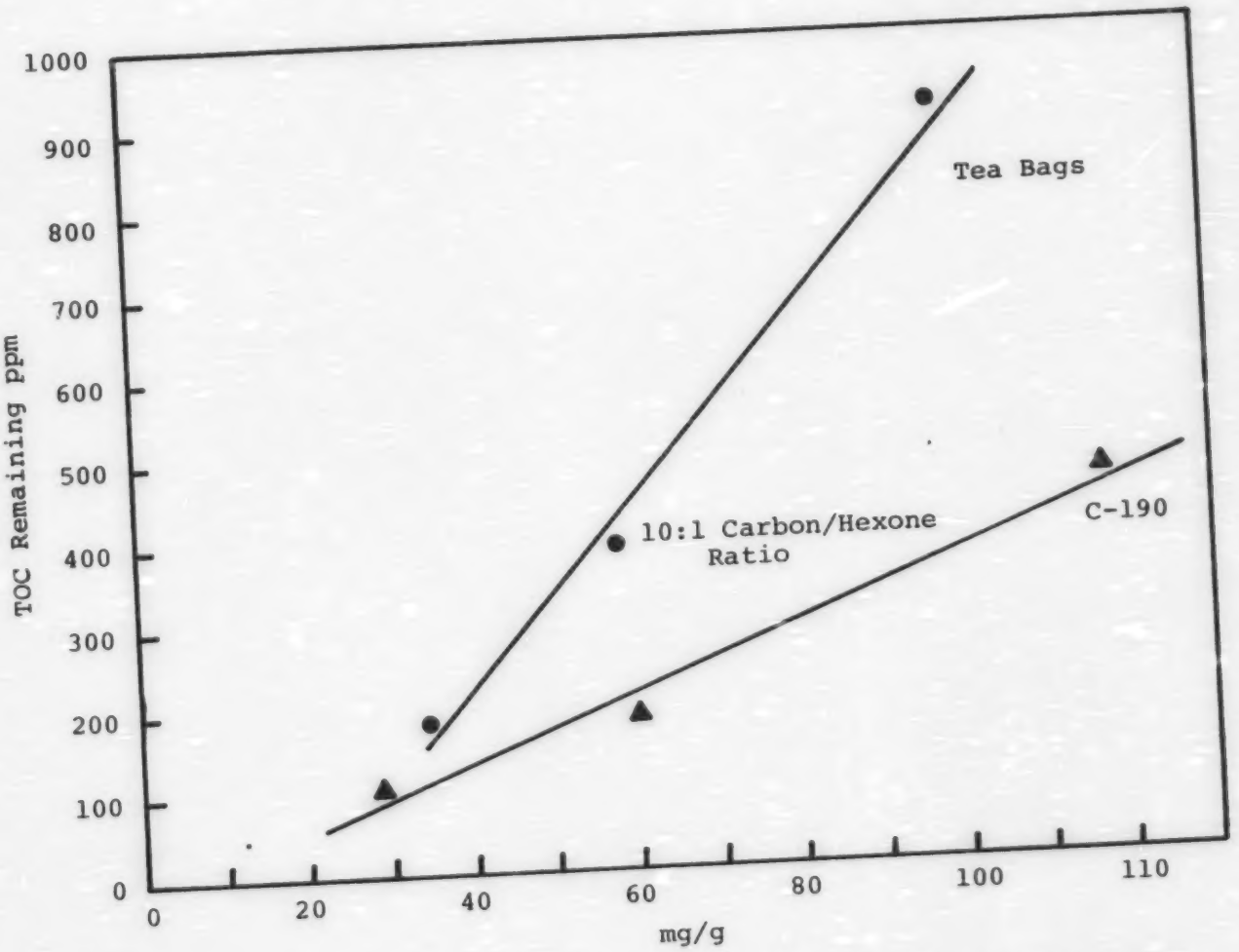

FIGURE 16. SORPTION CHARACTERISTICS FOR CARBON APPLICATION APPROACHES

30 minutes. Results were measured based on total organic carbon content. At an application of 10 to 1 carbon to hexone, theoretical limits are 80 percent removal for buoyant carbon and 60 percent for porous bags. At the same time, the buoyant carbon displays a greater potential for removal during a 30 minute agitation period than the porous bags. It is apparent that, kinetic difficulties associated with porous bag sorption increase contact requirements to more than 30 minutes.

A set of test runs was also conducted utilizing a greater spill volume and the same 10 to 1 carbon to hexone ratio. The latter was performed under the same operating procedures as previous investigations. Ten pounds of hexone solution were spilled instantaneously at the reservoir tailrace. Subsequently, 100 pounds (45.4 kg) of floating carbon or activated carbon in porous bags was added. The entire set, including the background run, was made at a flow rate of 10 cfs (283.2 liters). Results are compared to those standard runs at 10 cfs (283.2 liters) in Table 8.

Sampling anomalies continued to produce apparently erroneous estimates of removal at the upstream sampling sites, but final removal levels were comparable for high and low spill volumes in both approaches. It would appear that within the limits of this evaluation, size of the spill has little or no effect on removal efficiency for the flows tested here. A larger test facility would be required to better delineate effects of spill size. From the sorption characteristic data in Figure 16, one would expect better removal under circumstances where the sorption is more concentrated, i.e., closer to saturation.

TABLE 8

COMPARISON OF IN SITU TREATMENT EFFICIENCIES
AT LARGER SPILL VOLUME (FLOW RATE ∿10 CFS)

Spill Quantity (lbs)	Mode of Run	Hexone at Sample Site S (Total g)	Percent Remaining (Run/Bkgrd)	Hexone at Sample Site C (Total g)	Percent Remaining (Run/Bkgrd)	Hexone at Sample Site D (Total g)	Percent Remaining (Run/Bkgrd)
4	Background	1,441	100	2,265	100	2,135	100
4	Porous Bags	907	63	1,644	73	1,939	91
4	Floating	2,739	100+	1,783	100+	1,201	62
10	Background	5,350	100	5,337	100	5,316	100
10	Porous Bags	4,174	78	7,650	100+	4,711	89
10	Floating	6,740	100+	3,445	65	3,118	59

SECTION 9

PRACTICAL ASPECTS OF IN SITU TREATMENT IN FLOWING STREAMS

Field trials have shown that buoyant sorbents and, porous fiber bags, if given sufficient contact time, can be effective in removing organic materials spilled into flowing streams. Removal, however, is highly dependent upon the prompt location of the contaminant plume, even dispersion of media or bags over the surface, and favorable environmental conditions.

Wind will prove to be one of the major obstacles to efficient use of floating media or bags. Not only will air movement result in significant effects on the contact period, it can severely hamper collection efforts by herding the buoyant carbon or bags away from the boom. If aerial application is attempted, wind complications will be further amplified. It is also important to note that collection booms have a limited operation range and cannot deal with excessive currents ($\sim$5 knots). Therefore, quiescent or slower moving reaches of the stream must be sought for media retrieval.

Use of buoyant media also carries the potential for leaving unsightly carbon residuals along shorelines and beaches. Similarly, fiber bags may be left along the shore or hung up on shoals. While these effects were minimal during field trials, they must be considered prior to application in any public waterway.

The studies made to date suggest that removal efficiency will be greatly affected by scaling. Small spills such as those employed in the test program amplify the sensitivity to dosing and environmental considerations. Larger spills are marked by much larger spill plumes and higher concentrations. The dilute edges of the plume represent a much smaller percentage of the total spill. Therefore, removal in the center of the plume where the carbon is most efficient and where movement of the carbon does not separate it from the contaminated water is a greater part of the total removal. This indicates that average removal is likely to be much better on a larger scale than that noted in static water testing. A small acid spill in a semi-confined basin revealed very poor removal when compared to laboratory work. A much larger pesticide spill, however, resulted in removals comparable to those obtained in confined column work in the laboratory.[2] The edge and dilution effects become very

important as the size of the spill is reduced, and subsequently removal is less efficient in small scale applications.

While some of these factors suggest that removal may in fact be better than is suggested by field trials, one important feature of actual spills will complicate response greatly. That is the location and tracing of the contaminant plume. In the field trials, dye was used to facilitate accurate application. In the field, response personnel may find it very difficult to locate the spill and to define the boundaries of the plume. Thus, all the media could be applied in the wrong area and hence be totally ineffectual. This underscores the need for systems to monitor spills. Recent work with remote sensing devices and detection kits could satisfy this need.[7,8,9,10]

It has been noted that the hexone employed in the testing program to date has a tendency to stratify when released in water and, in so doing, complicates sampling. Volatility and reversible adsorption characteristics add to the uncertainty of analytical results. While these properties make hexone a difficult material to study carefully, it must be realized that they are shared by many hazardous substances and hence reflect real problems encountered in the field. Thus the data is complicated by incomplete recovery of all material and the necessity to look at apparent removal as opposed to absolute removal. The rhodamine dye, on the other hand, represents a conservative substance. It mixes well in the water, it undergoes no rapid degradation or volatilization, and it adsorbs onto the carbon with little apparent desorption. Removal is consequently much better for this substance (>95 percent versus 20-50 percent). Many hazardous substances will behave as the rhodamine dye when spilled and will therefore show much higher apparent removal efficiencies.

It is obvious that under no conditions will removal ever be complete. Therefore, one cannot assume that a response effort will eliminate a spill. It will only reduce its impact. Certain circumstances can be expected to maximize that reduction, and those are the cases where response should be promoted. From the observations made in this study, buoyant carbon is preferable to porous bags in the flowing stream system when contact times are very short (30 minutes) just as it was in static waters. Because the major difference appears to be one of kinetics, the longer contact times achievable in natural waters may change this somewhat.

Application of either buoyant carbon or porous bags may pose a logistics problem. Dr. Allen Jennings of the U.S. EPA Hazardous Substances Branch estimates that spills average 3,500 pounds (1.6 grams). At a ratio of 10:1 carbon to contaminant, this would require 35,000 (15.9 grams) of media or 17.5 tons (15.9 kg). If air transport is desired, this will require specialized

equipment. Larger spills may exceed the present transport capacity and thus suggest the potential use of containerized media supplied by shuttle to the response component.

All of the considerations offered here have bearing on the use of in situ response techniques on real spill events. They are pointed out to facilitate informed decisions about spill mitigation. Despite the restrictive nature of some of these observations, both the floating carbon approach and the porous bag approach are deemed promising for given spill scenarios. Present information needs center on the evaluation of these techniques under actual spill conditions.

REFERENCES

1. Shuckrow, A. J., B. W. Mercer and G. W. Dawson. "The Application of Sorption Processes for in situ Treatment of Hazardous Material Spills," in Proceedings of the 1972 National Conference on Control of Hazardous Material Spills, Houston, TX, March 21-23, 1972.

2. Mercer, B. W., A. J. Shuckrow and G. W. Dawson. "Treatment of Hazardous Material Spills with Floating Mass Transfer Media," U.S. Environmental Protection Agency, EPA-670/2-73-078, September 1973.

3. Mercer, B. W., A. J. Shuckrow and G. W. Dawson. "Application of Floating Mass Transfer Media to Treatment of Hazardous Material Spills," presented at the 46th Annual Water Pollution Control Federation Conference, Cleveland, OH, October 4, 1973.

4. Ziegler, R. C. and J. P. Lafornara. "In Situ Treatment Methods for Hazardous Material Spills," in Proceedings of the 1972 National Conference on Control of Hazardous Material Spills, Houston, TX, March 21-23, 1972.

5. Dawson, G. W. and M. W. Stradley. "A Methodology for Quantifying the Environmental Risks from Spills of Hazardous Material," presented at the AIChE Conference Boston-Sheraton, September 8, 1975.

6. Pilie, R. J., R. E. Baier, R. C. Ziegler, R. P. Leonard, J. G. Michalovic, S. L. Pek, and D. H. Bock, "Methods to Treat, Control and Monitor Spilled Hazardous Materials," U.S. Environmental Protection Agency, EPA 670/2-75-042, June 1975.

7. Kirsch, M. J. J. Vrolyk, R. W. Melvold, and J. P. Lafornara, "A Hazardous Material Spills Warning System" in Control of Hazardous Material Spills, Proceedings of the 1976 National Spills, Proceedings of the 1976 National Conference on the Control of Hazardous Material Spills, Information Transfer, Inc., Rockville, Maryland, April 1976.

8. Silvestri, A., A. Goodman, L. M. McCormack, M. Razulis, A. R. Jones, Jr., M. E. P. Davis, "Detection of Hazardous Substances" in Control of Hazardous Material Spills,

Proceedings of the 1976 National Conference on Control of Hazardous Material Spills, Information Transfer, Inc., Rockville, Maryland, April 1976

9. Silvestri, A., A. Goodman, L. M. McCormack, M. Razulis, A. R. Jones, Jr., M. E. P. David, "Development of a Kit for Detection of Hazardous Material Spills Into Waterways." Department of the Army, Edgewood Arsenal Special Publication ED-SP-76023, August 1976.